Second Harmonic Generation Indicates a Better Si/Ge Interface Quality for Higher Temperature and With N_2 Rather Than With H_2 as the Carrier Gas

V. K. Valev, M. K. Vanbel, B. Vincent, V. V. Moshchalkov, M. Caymax, and T. Verbiest

***Abstract*—In order for germanium (Ge) to replace silicon in advanced MOSFET channels, proper passivation of Ge is required. For this purpose, an ultrathin epitaxial Si cap was grown on Ge(001), and we applied second harmonic generation (SHG) in order to probe the Si/Ge interface quality. SHG indicates a better interface quality for a growth temperature of 500 °C rather than 450 °C. Similarly, a better quality of the interface is observed upon replacing the conventional H_2 carrier gas with N_2. Additionally, from the SHG signal, we were able to extract both the thickness of the native SiO_2 layer (∼4 monolayers (MLs)] and the thickness of the strained Si layer (relaxation at ∼12 MLs). These results are important for building Ge-based electronic components.**

***Index Terms*—Interface phenomena, MOSFETs, optics, semiconductor–insulator interfaces.**

I. Introduction

Nowadays, billions of MOSFETs are present on silicon (Si) microchips in electronic equipment and appliances. However, as device requirements are pushed forward, they encounter the fundamental limits of Si. Consequently, new materials with higher mobility than Si are being investigated for postsilicon technology.

Germanium (Ge) is one of the best substitutes. Ge presents important advantages over Si: It exhibits two times higher electron mobility and four times higher hole mobility. Additionally, it can be grown on Si substrates having the same crystalline structures, which eases its integration into existing devices. Unfortunately, however, the high chemical reactivity of Ge makes formation of native germanium oxide (GeO_X) unavoidable. Whereas germanium seems a better choice for the semiconductor part of the MOSFET, GeO_X is much more unstable compared with SiO_2.

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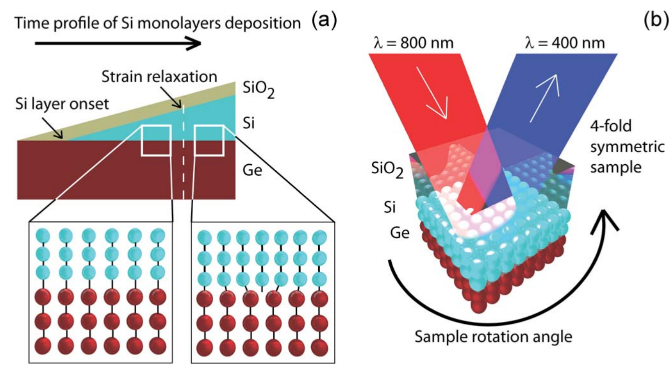

Fig. 1. (a) Silicon (Si) growth process. After exposure to the atmosphere, the top few MLs form a natural oxide (SiO_2). Because of the lattice mismatch, the first Si MLs on top of the Ge are strained. For thicker Si, the strain is released through formation of misfit dislocations. (b) Schematic of the surface/interface-specific SHG experiments. Upon rotating the sample, SHG probes the fourfold symmetry of the (001)-oriented Si and Ge lattices.

An ultrathin Si cap layer has been suggested as an efficient way to passivate the Ge surface and, henceforth, prevent it from oxidizing [1]–[4]. Within this method, the top few monolayers (MLs) of Si are partially oxidized to form an ultrathin SiO_2 layer, and subsequently, a high-k dielectric material can be deposited. Although this solution combines indeed the advantages of Ge and SiO_2/Si interlayers, its optimization requires the use of probing tools that are sensitive to the quality of buried interfaces.

Optical second harmonic generation (SHG) is well known for its surface/interface sensitivity down to the atomic layer, and in the past, it has been successfully used to characterize Si [5], [6]. Recently, we have applied SHG to the study of Si/Ge layers depending on Si precursor and temperature [7]. Here, we demonstrate that SHG can evaluate the quality of the buried Si/Ge interface as a function of temperature and carrier gas. These results are important for constructing Ge-based MOSFETs. Additionally, we demonstrate that SHG can define the inferior and superior limits for an efficient Si cap layer. These are the number of Si MLs that form SiO_2 and the number of Si MLs before creation of interface defects [see Fig. 1(a)]. The significance of these observations is best understood upon following the sample growth.

II. Sample Preparation and Characterization

The first part of the sample growth process produces clean Ge (001) surfaces. To this end, 200-mm Ge blanket wafers are obtained by first growing 1-μm Ge on Si substrates followed by chemicomechanical polishing, which removes about 300-nm germanium and yields smooth Ge surfaces (root mean square (RMS) $= 0.2-0.4$ nm and $Z_{\max} = 5$ nm determined by atomic force microscopy). In order to remove germanium native oxide prior to Si growth, the Ge surfaces receive a HF clean and an *in situ* bake at 650 °C, under H_2.

Next, pure ultrathin Si caps are grown, i.e., with minimal Ge surface segregation into Si. The caps are deposited in an ASM-Epsilon RPCVD reactor. Trisilane (Si_3H_8) is used as the Si precursor because it allows Si growth at very low temperature (below 500 °C) [8] and strongly limits Ge surface segregation [9]. Si thickness is measured by spectroscopic ellipsometry immediately after growth and is converted in MLs, whereby 1 ML $=$ 0.13 nm. It should be noted that, upon exposure to the ambient, the top few Si MLs form a natural oxide [see Fig. 1(a)]. As the thickness of the unoxidized Si layer increases, the 4.2% lattice mismatch with the underlying Ge causes an increase in stress within the first few Si MLs. For larger Si thickness, this strain is released through misfit dislocations, whereby Si dangling bonds appear at the interface. Upon completion of the growth process, the samples are ready to be measured with SHG.

The SHG experiments are performed with a Ti:sapphire laser at an 800-nm fundamental wavelength and with a standard setup. Because the sample surface has a fourfold symmetry, we can expect a fourfold symmetric expression in the equations describing the SHG signal as well.

III. Theoretical Specifications

For a (001)-oriented lattice, in the $S_{\rm IN}-P_{\rm OUT}$ polarizer–analyzer configuration, we can calculate the SHG intensity by means of Sipe's theoretical model [10], i.e.,

$$\begin{aligned} I_{S_{\rm IN}-P_{\rm OUT}}(2\omega) &\propto \left|P^D_{\rm iso} + P^Q_{\rm iso} + P^Q_{\rm anis}\sin^2 2(\phi+\theta)\right|^2 \\ &\propto |I_0(2\omega)| + 2|C|\sin^2 2(\phi+\theta) + \cdots \end{aligned} \tag{1}$$

where $P^D_{\rm iso}$, $P^Q_{\rm iso}$, and $P^Q_{\rm anis}$ are the nonlinear polarizations, which can be dipolar (superscript D), quadrupolar (superscript Q), isotropic (subscript iso), and anisotropic (subscript anis). Additionally, ϕ is the angle of sample rotation, and θ is the phase. Furthermore, $I_0(2\omega) = (P^D_{\rm iso} + P^Q_{\rm iso})^2$, whereas $C = 2(P^D_{\rm iso} + P^Q_{\rm iso})P^Q_{\rm anis}$, and we neglected the term to the power of 4 because the isotropic contributions are much larger than the anisotropic one. Indeed, in our samples, the latter was evaluated alone, in the $S_{\rm IN}-S_{\rm OUT}$ polarizer–analyzer configuration, and for all samples, the signal was found to be less than 20 counts/s, $P^Q_{\rm anis}$ regroups all constant terms, ϕ is the angle of sample rotation, and θ is the phase.

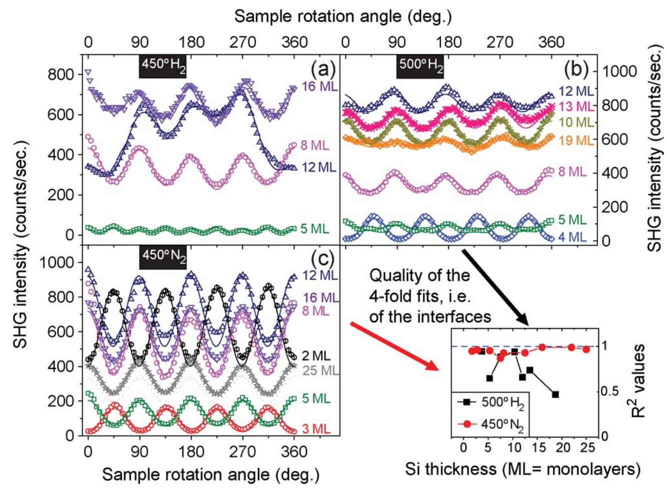

Fig. 2. (a) Upon deposition of the Si MLs at 450 °C with H_2 as the carrier gas, the interface-specific SHG yields an irregular response that indicates a poor quality of the Si/Ge interface. (b) Rising the temperature or (c) switching to N_2 as the carrier gas dramatically improves the quality of the interface. While fitting the SHG response to the fourfold symmetry of a (001)-oriented Si/Ge interface is impossible for (a), the inset shows that, in (c), the fits are better than in (b); therefore, the interface quality is highest in (c). All data were measured in the $S_{\rm IN}-P_{\rm OUT}$ polarizer–analyzer configuration.

IV. Results

Equation (1) describes the SHG signal from an ideal surface or interface. However, large interdiffusion, roughness, defects, etc., could lower the quality of the interface. Therefore, fitting the experimental data to (1) provides a measure of interface quality: High-quality interfaces will fit well, poorer ones will not.

For the purpose of optimizing the interface quality during the growth process, we studied the influence of temperature (450 °C versus 500 °C) and carrier gas (H_2 versus N_2). We believe that while temperature affects the dynamics of the growth mechanism, the carrier gas determines its nature. Indeed, the presence of H_2 insures good surface H passivation of Ge, and henceforth, during growth, Si atoms must take the place of H atoms. In a different manner, the presence of N_2 might result in poorer H surface passivation of Ge, and henceforth, during growth, Si atoms can bind to Ge at vacancy sites, i.e., without displacing H atoms.

In Fig. 2(a), the SHG response as a function of sample rotation angle can be seen for samples that were grown at 450 °C with H_2 as the carrier gas. For 5 MLs of Si, the material is mostly oxidized, and there is no real Si/Ge interface. For 8, 12, and 16 MLs, fitting the graphs with (1) alone is impossible. Both increasing the temperature [see Fig. 2(b)] and changing the carrier gas [see Fig. 2(c)] dramatically improve the interface quality. Indeed, all the graphs in these figures can be fitted with(1), and as shown in Fig. 2 (inset), the best fits are obtained upon switching to N_2 as the carrier gas. Furthermore, the fitting parameters themselves contain interface-specific information.

In Fig. 3(a), the intensity term $I_0(2\omega)$ from (1) is plotted as a function of the deposited Si thickness, for both the growing conditions at 500 °C with H_2 and at 450 °C with N_2. Both curves indicate clear extrema that are associated with the

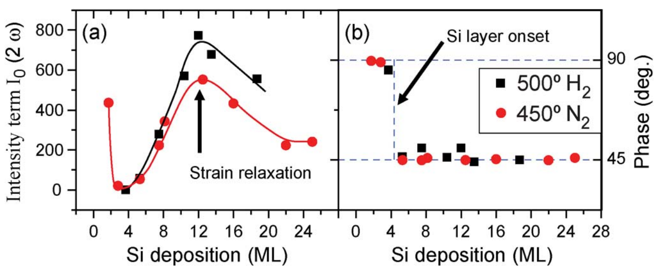

Fig. 3. Fitting the interface-specific SHG curves in Fig. 2 to a fourfold symmetrical response yields the (a) intensity term $I_0(2\omega)$ and (b) phase term θ. Plotting these parameters as a function of the number of deposited Si MLs clearly reveals the onset of Si layer growth and the strain relaxation.

interface events of Si layer onset and strain relaxation [see also Fig. 1(a)]. More specifically, from the point of view of an interface-specific technique such as SHG, the appearance of new interfaces within the sample is a dramatic event. A large change in the signal is therefore expected for a Si thickness of 4–5 MLs, since this is the depth of SiO_2, as measured by ellipsometry after native oxide formation (see also [7]) Moreover, the signal from the Si/Ge interface is opposite in phase to the signal from the SiO_2/Si interface because these interfaces have opposite orientations (directions of the surface normal) with respect to Si. Additionally, for the purpose of comparing the SHG signal before the Si layer onset and afterward, we consider that the oxide/semiconductor interfaces SiO_2/Si and SiO_2/Ge are similarly oriented. Therefore, when the signals from both SiO_2/Si and Si/Ge interfaces cancel, the total SHG amplitude is zero. However, how thick should the Si be for this cancellation?

We can find the answer in Fig. 3(b), where the total SHG phase θ in (1) is plotted as a function of the thickness of deposited Si. It can be seen that, within a thickness of 2 MLs, the phase reverses completely, which indicates that 2 MLs of Si are all that is needed for the amplitude $I_0(2\omega)$ to cancel. Both the amplitude minimum and the phase change are therefore clear indicators for the onset of the Si layer. Subsequently, as the thickness of the Si layer increases, the two Si interfaces move away from complete cancellation, and henceforth, the SHG signal increases until the maximum of $I_0(2\omega)$ is reached.

With increasing Si thickness, the contribution from the lower interface should eventually decrease due to absorption in Si for both the fundamental and the second harmonic. However, the absorption in Si is negligible for a thickness of 7–8 MLs. On the other hand, strain relaxation in Si, together with formation of misfit dislocations at the Si/Ge interface, is expected to occur in the range from 0.8 to 1.5 nm [2], [3], [11]. This indicates that the maximum of $I_0(2\omega)$ at 12 MLs (~1.5 nm) is indeed related to strain relaxation.

V. Conclusion

In conclusion, we have demonstrated that SHG is a valuable tool to evaluate the quality of the Si/Ge interfaces, which is particularly useful for optimizing ultrathin Si cap growth on Ge. In our case, the influence of carrier gas and temperature was studied, but other growth parameters with an impact on the interface can be investigated as well (i.e., nature of the Si precursor, crystalline orientation, preparation of the Ge surface, and film contamination, etc.). In the past, SHG has been widely applied in the study of Si surfaces. Surfaces, however, can readily be investigated at the atomic scale with surface probe microscopes. Therefore, our work shows that SHG is even better suited for the study of buried semiconductor interfaces for next-generation devices.

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